



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A23L 1/304, 1/0524, A23C 9/152, 9/154, 9/13, 9/137	A1	(11) International Publication Number: WO 98/18349 (43) International Publication Date: 7 May 1998 (07.05.98)
(21) International Application Number: PCT/EP97/05192 (22) International Filing Date: 22 September 1997 (22.09.97) (30) Priority Data: 08/739,070 28 October 1996 (28.10.96) US (71) Applicant: SOCIETE DES PRODUITS NESTLE S.A. [CH/CH]; P.O. Box 353, CH-1800 Vevey (CH). (72) Inventors: REDDY, Sekhar, 2 Briar Lane, New Milford, CT 06776 (US). JACOBSON, Mark, Randolph; 27 Candlewood Springs, New Milford, CT 06776 (US). VADEHRA, Dharam, Vir; 6 Hallets Road, New Milford, CT 06776 (US). WEDRAL, Elaine, Regina; Chestnut Hill Road, R.R.2, P.O. Box 480 A, Sherman, CT 06784 (US). (74) Agent: PATE, Frederick, George; Avenue Nestlé 55, CH-1800 Vevey (CH).		(81) Designated States: AL, AM, AU, AZ, BB, BG, BR, BY, CA, CN, CZ, EE, ES, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LV, MD, MG, MK, MN, MW, MX, NZ, PL, RO, RU, SD, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: FORTIFICATION OF FOOD WITH A COMPLEX OF CALCIUM (57) Abstract <p>A fortified foodstuff comprising a fortifying amount of a complex of calcium and a hydrolysed polysaccharide. The foodstuff may be a dairy-based product such as milk or a milk product.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

FORTIFICATION OF FOOD WITH A COMPLEX OF CALCIUM

FIELD OF THE INVENTION

- 5 The present invention relates to the fortification of food and more particularly to the fortification of food with calcium.

BACKGROUND OF THE INVENTION

- 10 Calcium is an important element in human diets for adequate bone formation and maintenance as well as other metabolic functions, e.g. nerve transmission, blood clotting, proper cell function and muscle contraction. It is common practice to fortify food products with calcium sources which are either insoluble or soluble at around neutral pH. Many of the calcium sources currently used for fortification
15 which are insoluble or substantially insoluble at around neutral pH, e.g. calcium carbonate, calcium phosphates, calcium citrate and other organic acid salts of calcium, result in precipitation and a chalky mouth feel. Other calcium sources which are soluble or substantially soluble at around neutral pH such as calcium chloride, calcium hydroxide and a few organic acid salts of calcium react with
20 milk proteins resulting in undesirable coagulation and sedimentation.

- It is also common practice to stabilize or reduce the sedimentation of the calcium and milk proteins in the milk beverages fortified with calcium sources by adding carrageenans, pectins and/or other gums, but such materials impart an undesirably
25 high viscosity to milk. Protein destabilisation, e.g. precipitation and coagulation, is mainly attributed to free calcium ions in the system.

- It would be highly desirable to have a calcium source to fortify milk beverages and other dairy based products without coagulation and sedimentation, with improved
30 palatability.

SUMMARY OF THE INVENTION

- 35 We have developed a complex of calcium and a hydrolysed polysaccharide which may be added to a foodstuff to fortify it with calcium to provide a stable foodstuff, without coagulation and sedimentation, which has improved palatability.

According to the present invention, there is provided a fortified foodstuff comprising a fortifying amount of a complex of calcium and a hydrolysed polysaccharide.

5

The foodstuff may be a dairy based product such as a milk beverage, a confectionery product, ice cream or another beverage such as a juice.

The complex may consist of calcium and a hydrolysed polysaccharide alone or together with an acid.

10

DETAILED DESCRIPTION OF THE INVENTION

The hydrolysed polysaccharide may be derived from a negatively charged polysaccharide, e.g. carboxymethylcellulose, gums or carrageenans but it is advantageously a hydrolysed pectin. Pectins typically have a molecular weight of 10,000 to 150,000 with a Degree of Polymerisation (DP) of 50 to 800 and are methoxylated from 20 to 80%. Although pectins may theoretically be hydrolysed to a DP of 1 and demethoxylated to 0%, these levels are difficult to achieve.

Preferably, the hydrolysed pectin has an average DP of from 1 to 25 and more preferably from 1 to 10. The hydrolysed pectin is conveniently demethoxylated to more than 50% and preferably more than 75%.

15

20

The hydrolysis (and the demethoxylation when the polysaccharide is pectin) may be carried out by chemical, physical or enzymatic means or any combination thereof. The enzymatic hydrolysis may be carried out, for instance, by a process as described in our co-pending US Patent Application (NO5387/39). The chemical hydrolysis may be carried out by treatment with an acid but is preferably carried out by treatment with an alkali. The physical hydrolysis may be carried out by shear.

25

30

The complex of calcium and the hydrolysed polysaccharide may be prepared by mixing an aqueous solution or suspension of a calcium compound with an aqueous solution or suspension of a hydrolysed polysaccharide. The calcium compound may be calcium hydroxide or it may be derived from one or more of several salts, e.g. the chloride, carbonate, phosphate, sulfate or citrate. When the

35

complex consists of calcium and a hydrolysed polysaccharide together with an acid, the acid is preferably an organic acid, e.g. citric, malic, fumaric, tartaric, succinic or lactic acid. One or more acids may be used if desired.

- 5 The complex is formed as an aqueous solution or suspension and, if desired, may be dried, for instance to a powder, by various methods commonly known to those skilled in the art.

- 10 The fortified foodstuff comprising a fortifying amount of a complex of calcium and a hydrolysed polysaccharide may be prepared by mixing the foodstuff with the complex. The complex may be in the form of a solution or suspension or it may be in a dry form such as a powder.

- 15 The amount of complex present in the fortified foodstuff may be from 0.05 to 5%, preferably from 0.1 to 2.5%, and more preferably from 0.2 to 1.0% by weight based on the weight of the foodstuff.

- 20 The foodstuff may subsequently be further stabilised by adding gums, e.g. carrageenans, gum arabic, guar gum, etc., or by adding emulsifiers, e.g. mono- or di-glycerides, lecithin, sodium stearyl lactate, or the citric acid ester of monoglyceride

The fortified foodstuff may be frozen, refrigerated or shelf-stable.

25 **EXAMPLES**

The following examples further illustrate the present invention.

Example 1

30

Two solutions/suspensions are prepared:

- A. 1.8g calcium chloride in 10mL water
B. 4.0 grams of pectin hydrolysates consisting of approximately 77% DP 1-3 (the
35 remainder being primarily insoluble matter and moisture) in 40mL water.

The solutions/suspensions are mixed and then added to 940mL skim milk. The milk is then homogenised and pasteurised, and stored in a refrigerator at 2-5°C. The milk was found to be stable, without sediment and of good flavour after 7 weeks.

5

Example 2

Three solutions/suspensions are prepared:

10

A. 1.2g calcium chloride in 10mL water

B. 2.071g citric acid in 10mL water

C. 4.0 grams of pectin hydrolysates consisting of approximately 77% DP 1-3 (the remainder being primarily insoluble matter and moisture) in 40mL water.

15

The solutions/suspensions A and B are mixed, then solution C is added. The final mixture is then added to 940mL skim milk. The milk is then homogenised and pasteurised, and stored in a refrigerator at 2-5°C. The milk was found to be stable, without sediment and of good flavour after 7 weeks.

20

Example 3

Fortified milk is prepared as in Example 2 except that instead of being pasteurised, it is ultra high temperature treated (UHT). After being stored in a refrigerator at 2-5°C for three weeks, the milk was found to be stable, without sediment and of good flavour.

25

CLAIMS

1. A fortified foodstuff comprising a fortifying amount of a complex of calcium and a hydrolysed polysaccharide.
2. A fortified foodstuff according to claim 1 wherein the foodstuff is a dairy based product, a confectionery product, ice cream or a beverage.
3. A fortified foodstuff according to claim 1 wherein the complex consists of calcium and a hydrolysed polysaccharide together with an acid.
4. A fortified foodstuff according to claim 1 wherein the hydrolysed polysaccharide is a hydrolysed pectin.
5. A fortified foodstuff according to claim 4 wherein the hydrolysed pectin has a DP of from 1 to 25.
6. A fortified foodstuff according to claim 4 wherein the hydrolysed pectin is demethoxylated to more than 50%.
7. A fortified foodstuff according to claim 1 wherein the amount of complex present in the fortified foodstuff is from 0.05 to 5% by weight based on the weight of the foodstuff.
8. A fortified foodstuff according to claim 1 which is frozen, refrigerated or shelf-stable.
9. A process for preparing a fortified foodstuff comprising a fortifying amount of a complex of calcium and a hydrolysed polysaccharide which comprises mixing the foodstuff with the complex.
10. A process according to claim 9 wherein the complex is in the form of a solution or suspension or a dry form.
11. A fortified foodstuff according to claim 1 wherein there is also added a gum and/or an emulsifier.

INTERNATIONAL SEARCH REPORT

Inter national Application No
PCT/EP 97/05192

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A23L1/304 A23L1/0524 A23C9/152 A23C9/154 A23C9/13
A23C9/137

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A23L A23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 9212 Derwent Publications Ltd., London, GB; Class B04, AN 92-092875 XP002054300 -& JP 04 036 166 A (POLA CHEM IND INC) , 6 February 1992 see abstract ---	1-6
X	DATABASE WPI Section Ch, Week 9342 Derwent Publications Ltd., London, GB; Class A96, AN 93-331359 XP002054301 -& JP 05 238 940 A (POLA CHEM IND INC) , 17 September 1993 see abstract --- -/--	1-6

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

3 February 1998

Date of mailing of the international search report

17.02.98

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Van Moer, A

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 97/05192

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: none
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
"A complex of calcium and a hydrolysed polysaccharide " is not precise enough for a complete search to be performed.
The search has been limited to the complexes as described page2, lines 17-22 and in the examples.

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 97/05192

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 235 971 A (BORDEN) 9 September 1987 see claims	1-11
A	EP 0 715 812 A (YAKULT) 12 June 1996 see claims	1-11

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/EP 97/05192

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 235971 A	09-09-87	US 4701329 A	20-10-87
		AU 581146 B	09-02-89
		AU 6091486 A	13-08-87
		BR 8700569 A	08-12-87
		CA 1292636 A	03-12-91
		JP 62248450 A	29-10-87

EP 715812 A	12-06-96	JP 8154575 A	18-06-96
		AU 4026195 A	13-06-96
		US 5609898 A	11-03-97

THIS PAGE BLANK (USPTO)